Final Report

Development of large capacity Lead-Carbon Hybrid Ultracapacitors for energy harvesting and storage

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14. ABSTRACT
Hybrid ultracapacitors (HUCs) are a new class of emerging electrochemical energy storage devices. Among various hybrid ultraultracapacitors, PbO2 ? Activated Carbon is an attractive system owing to its high cell voltage that provides it both high energy and power densities. In this project, we have designed and developed 12V / kF-range Lead-Carbon (LC) HUCs with absorbent-glass-mat (AGM) and silica-gel electrolyte configurations and tested their performance. The capacitance for the HUC in silica gel electrolyte configuration is found to be higher than AGM configuration because the enhancement of active surface area of positive plate and the effect of polymeric structure of silica gel on negative plate. The constant-power discharge curves show that lead-carbon HUCs have the capability to deliver energy as well as power for specified time duration. This dual feature of energy and power is a clear advantage of having a battery type electrode and a capacitor type electrode.

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ultra capacitors, ultra capacitors, power storage, power storage, Magneto-optical imaging , Magneto-optical imaging , lead oxide activated carbon

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. In this project, we have designed and developed 12V / kF-range Lead-Carbon (LC) HUCs with absorbent-glass-mat (AGM) and silica-gel electrolyte configurations as shown in Fig. 1 and have performance tested them.

Details on preparation of electrical double-layer carbon electrodes, substrate-integrated PbO_2 (referred as Lead) electrodes, and assembly of lead-carbon ultracapacitor devices are given below.

Preparation of activated-carbon electrodes

5 wt. % of Poly(vinylidenefluoride) (PVDF) polymer was dissolved in required quantity of Dimethylformamide (DMF) solvent by ultrasonication for 15 mins. Subsequently, 85 wt. % of high surface area (~1512 m^2/g) amorphous carbon (Meadwestvaco carbon X-090177) and 10 wt. % of activated charcoal AR (~ 974 m^2/g) (s d fine-chem Ltd., Mumbai-400030, India) were dispersed into the PVDF-DMF solution to obtain a thick carbon-ink which was applied onto 1 mm thin graphite sheets with geometrical area was of 172.5 (11.5 cm x 15 cm) sq. cm and the tag dimensions were of 1.5 cm x 1.5 cm x 1 mm. Weight of the graphite electrode was ~ 40 g. Each side of the graphite current collector was contained by ~ 3 g carbon. Graphite electrodes were subsequently dried in an air oven at 80 ^oC for 6-8 h.

Preparation of substrate-integrated PbO_2 (Lead) electrodes

Substrate-integrated PbO_2 electrodes were prepared from lead sheets (99.9% purity) of dimensions 11.5 cm x 15 cm x 0.3 mm with tag dimension of 1.5 cm x 1.5 cm x 0.3 mm weighing ~ 90 g. Lead sulphate formed on the lead sheets after overnight dipping in 6 M aq. H_2SO_4 was converted to PbO_2 by constant-current charging at 1 mA cm^{-1}. Five consecutive charge-discharge cycles at 1 mA cm^{-1} provided the capacity of Substrate-integrated PbO_2

electrodes were 1 mAh cm^{-1}. These electrochemically formed Substrate-integrated PbO_2 electrodes were used as positive plates in HUCs.

Assembly of 12 V / kF- range HUC

12 V HUCs with activated carbon electrodes sandwiched between substrate-integrated PbO_2 electrodes were assembled in AGM configuration in 6 M aq. sulphuric acid or silica gel with 1.4 g/cc aq. sulphuric acid using a commercial six-compartment 12 V/ 42 Ah lead-acid battery containers. Accordingly, HUCs comprised six hybrid ultracapacitors with appropriate number of electrodes connected in series. Each compartment was containing seven positive plates and six negative plates in parallel connection. Capacitors unit were filled by absorbent-glass-mat (AGM) socked with adequate aq. H_2SO_4 electrolyte, or silica gel-electrolyte. The weights of two devices are ~10 kg. HUCs were performance tested using a Bitrode instrument fitted with a LCN-Power Module. A. C. impedance studies were carried out by using Autolab Potentiostat/Galvanostat-Model 30 in conjunction with a voltage multiplier.

Constant current charge-discharge testing

12 V HUCs were performance tested by constant current charge-discharge at varying currents. Two ranges of current value was selected, lower range values like 3, 6, 9, 12, 15 A and higher range values like 25, 50, 75, 100 A. Each cases capacitance values (C) were calculated from the ratio of negative slopes of discharge profiles and the corresponding currents. From the basic understanding one can write, Q = C x V, where Q is the charge on the electrodes and V is the voltage difference between the electrodes. Since Q = I x t, where I and t represent current and time, respectively. Accordingly, V = $\frac{\mathrm{Ixt}}{\mathrm{C}}$, and by differentiating with respect to time at constant current, we get, $\frac{dV}{dt} = \frac{I}{C}$. During the constant current charge-discharge of HUCs, voltage varies almost linearly with time. The charging profiles have

positive slope of I/C while discharge profiles have negative slope of –I/C. In practical situation, during the discharge of HUCs, there will be an initial voltage drop due to the internal ohmic resistance, called as IR drop, where R is the ohmic resistance. Since this IR drop is not fesiable for capacitive discharge, the capacitance values were calculated excluding both ESR (equivalent series resistance) and EDR (electrical double-layer resistance).

In this study HUCs were subjected to constant currents charge to a cut-of-voltage of 13.8 V followed by potentiostatic charge at 13.8 V for 1 h. Then constant currents discharge up to 6 V. The capacitance values at 3 A current (C-rate for the positive electrode) are 1.38 kF and 2.45 kF which decrease to 1.25 kF and 2.31 kF at a discharge current of 15 A (5-C rate for the positive electrode) for AGM and silica gel electrolyte configurations, respectively. At the higher current values (e.g. 25, 50, 75, 100 A) capacitance again decreases. All of the discharge profiles of HUCs at constant currents are shown in Fig. 2 (a, b) and 3 (a, b). The capacitance for the HUC in silica gel electrolyte configuration is found to be higher than AGM configuration because the enhancement of active surface area of positive plate and the effect of polymeric structure of silica gel on negative plate.

Temperature dependence of capacitance

The trend for change in the capacitance values at varying temperatures are different for AGM and silica gel HUCs as shown in Fig. 4 (a, b). The capacitance is found to decline with decreasing temperature, due to the lowering of electrolyte conductivity and freezing of electrolyte below zero degrees centigrade. The working temperature range of HUC is too wide from -30 to 50 °C that it can be used at any feasible environment.

Faradaic efficiency determination

Faradaic efficiencies of HUCs, AGM and silica gel electrolyte configuration, were calculated from constant current charge-discharge at 3A current. From Fig 5 the efficiency values are indicated as 93 % and 92 % for AGM and gelled electrolyte HUC respectively. The high faradaic efficiency is achieved mainly for using activated carbon capacitor electrode as negative plates and this is one of the attractive features of the Substrate-integrated lead-carbon hybrid ultracapacitors.

Constant power discharge data

Constant-power discharge curves at 10, 20, 30, 40 and 50 W for 12 V lead-carbon HUCs are shown in Fig.6 (a, b). HUCs were first charged by constant current at 0.3A up to a cut-of-voltage of 13.8 V followed by 1 h potentiostatic charging at 13.8 V. During the constant-power discharge of the HUCs, the current is found to increase as the voltage decreases. The constant-power discharge curves show that lead-carbon HUCs have the capability to deliver energy as well as power for specified time duration. This dual feature of energy and power is a clear advantage of having a battery type electrode and a capacitor type electrode.

Impedance study

Internal resistance measurements have been done using A. C. impedance spectroscopy at different state-of-charge (at different voltage) of the HUCs. The x-intercept value at high frequency region in the Nyquist plot indicates the resistance value, shown in Fig.7. Response time is another important parameter of HUCs which can be estimated from bode plot (phase vs. frequency) using A. C. impedance spectroscopy. In Bode plot the resistance and capacitive reactance are equal at -45° phase angle; the corresponding frequency called as

breaking frequency. Beyond this frequency capacitive reactance become larger than resistance. The time corresponding to the breaking frequency is represented as response time of the capacitor. The response times for the HUCs are estimated to be 1.66 s and 4.68 s for the AGM and gel electrolyte configurations, respectively shown in Fig.8 (a, b). These lower response times indicate the effective pulse power applications of the HUCs.

Energy density and power density calculations

Battery is recognised as an energy device and capacitor as a power device. But as substrate-integrates lead-carbon HUC devices are overarch of these two, the energy density and power density are the curtail components for its applications. These two are estimated from the constant power discharge profiles of HUCs. Energy values can be calculated from discharge plots by the multiplication of the discharge times and the corresponding powers. Energy density is the normalised form of calculated energy by the total weight of HUCs. To calculate the power density the response time is an important factor that can be known from the impedance study. Power density is nothing but the ratio of energy density and the response time. The energy and power densities of HUCs are summarized in Table 1.

Self-discharge, leakage current and parallel resistance measurement

In the present study, self-discharge for the HUCs was measured after charging them potentiostatically for 3h at 13.8 V followed by 24 h in open-circuit condition at room temperature (28^{o}C) and 50°C shown in Fig 9 (a, b). It is observed that at higher temperature, the self-discharge is only marginally increased. Self-discharge data accumulation was also conducted for seven days at room temperature shown in Fig 9 (c). 'Self-discharge energy loss factor (SDLF)' was calculated from the voltage loss data with respect to time according to the following equation.

$$(SDLF) = 1-(V/V_w)^2$$

Whereas V and V_w are the voltage after measured time and the working voltage [8]. Self-discharge for the gelled configuration is higher than the AGM configurations. As the self-discharge is higher for gelled system, the leakage current also is higher while parallel resistance is lower for it. Leakage current was measured during 24 h after fixing the voltage at 13.8 V. Parallel resistance after 24 h was obtained as a ratio of working voltage, i.e. 13.8 V, and leakage current after 24 h. Self-discharge, leakage current and parallel resistance values for AGM and gelled HUCs are given in Table 2. It is noteworthy that the enhancement in active surface area of PbO_2 active material is ads up to self-discharge of HUC in gel configuration.

Pulse- cycling data

12 V substrate-integrated lead-carbon HUCs were subjected to pulsed cycle-life test under charge-discharge current load of 30 A, at first 50,000 cycles for duration of the 1 s followed by rest for 5 s. The effect of high-rate pulsed cycling on the capacitance of these HUCs was also studied. 50,000 cycling with 60 A charge-discharge pulse rates for 1 s followed by 10 s rest were also performed. The capacitance measurements were carried out at 3 A current discharges after each 10,000 cycles and data are shown in Fig. 10. After 100,000 cycles the capacitance loss are calculated as 36 % and 23 % for AGM and gelled HUCs respectively. The enhanced cycle-life of the HUCs are mainly attributed for the coupling of the capacitor electrode with the battery type electrode. This data is truly attractive for the long term applications of HUCs.

Table 1. Energy density and power density data for AGM and gelled HUCs.

	Energy Density / Wh kg^{-1}	**Response Tome / s**	**Power Density / W kg^{-1}**
AGM	0.9	1.66	1937
Gel	1.8	4.86	1333

Table 2. Self-discharge, leakage current and parallel resistance data for AGM and gelled HUCs.

Parameter	**AGM**	**Gel**
Self-discharge at room temperature for one day (28 ^{o}C) / %	15	18
Self-discharge at 50 ^{o}C for one day / %	19	22
Self-discharge at room temperature for seven days (28 ^{o}C) / %	23	26
Leakage Current / mA	80	180
Parallel Resistance / Ω	173	77

Figure captions

Fig. 1. Photograph of a 12V/kF-range LC HUC.

Fig. 2: Constant current discharge profiles at varying current loads (3, 6, 9, 12, 15A) (a) AGM, (b) gelled HUCs.

Fig. 3: Constant current discharge profiles at varying current loads (25, 50, 75, 100A) (a) AGM, (b) gelled HUCs.

Fig. 4: Capacitance study at variable temperatures for (a) AGM, (b) gelled HUCs.

Fig. 5: Constant current charge-discharge profiles of HUCs.

Fig. 6: Constant power discharge profiles at varying power loads (a) AGM, (b) gelled HUCs.

Fig.7: Resistance vs. potential profiles for HUCs. Inset: Nyquist plots of AGM and gelled HUCs.

Fig. 8: Response time measurement plots for (a) AGM, (b) gelled HUCs.

Fig. 9: Self-discharge profiles of HUCs (a) one day at room temperature, (b) one day at 50 °C, (c) Seven days at room temperature; Inset: Percentage of voltage loss vs. time plot.

Fig. 10: Cycle life test data for HUCs.

NED
ENERGY LIMITED
PbO2-AC Hybrid Ultracapacitor
12V / 1 kF
Solid State and Structural Chemistry Unit
Indian Institute of Science
Bangalore – 560012
and
NED Energy Limited, Hyderabad.
12V / kF-range Lead-Carbon HUCs

Fig. 1

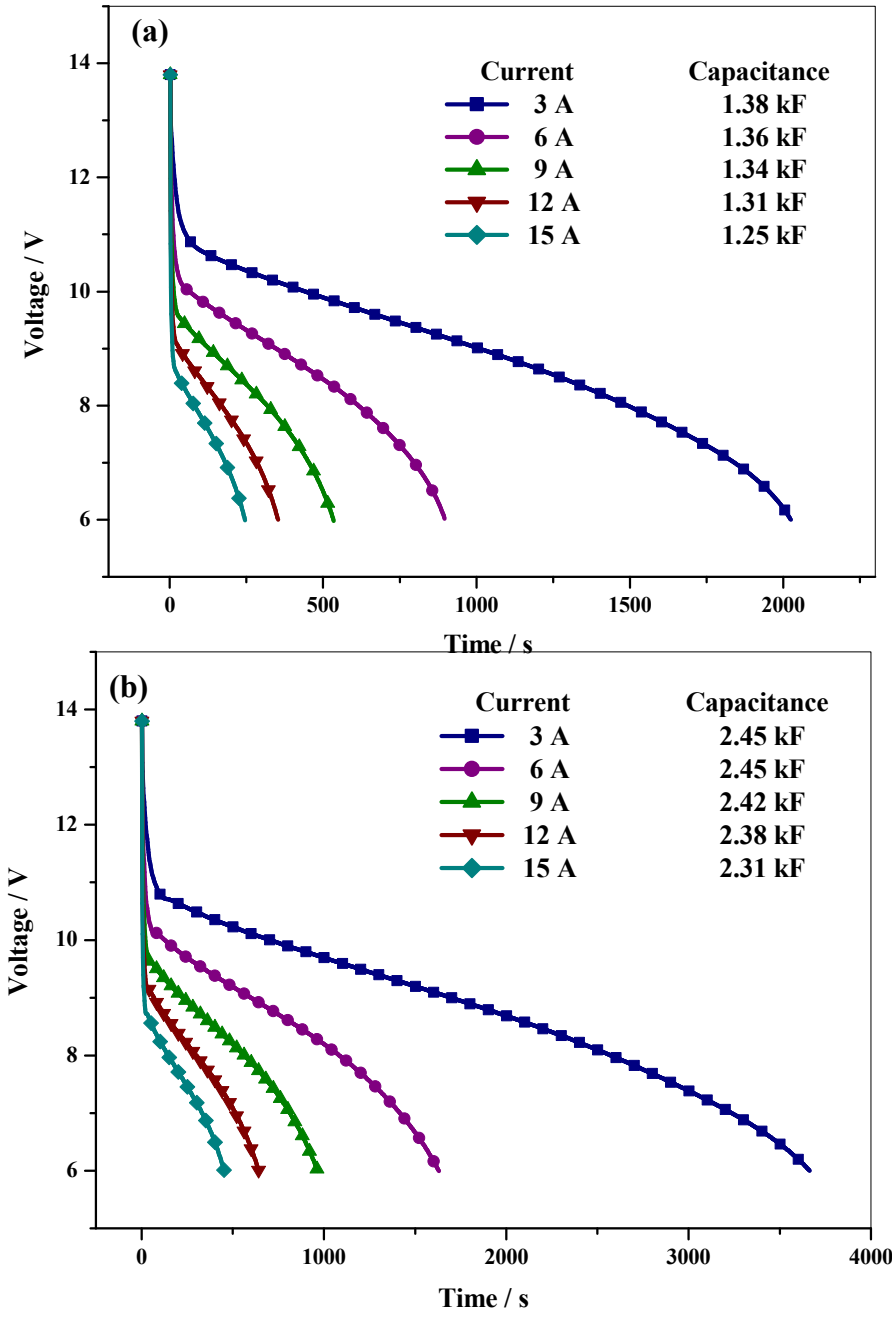
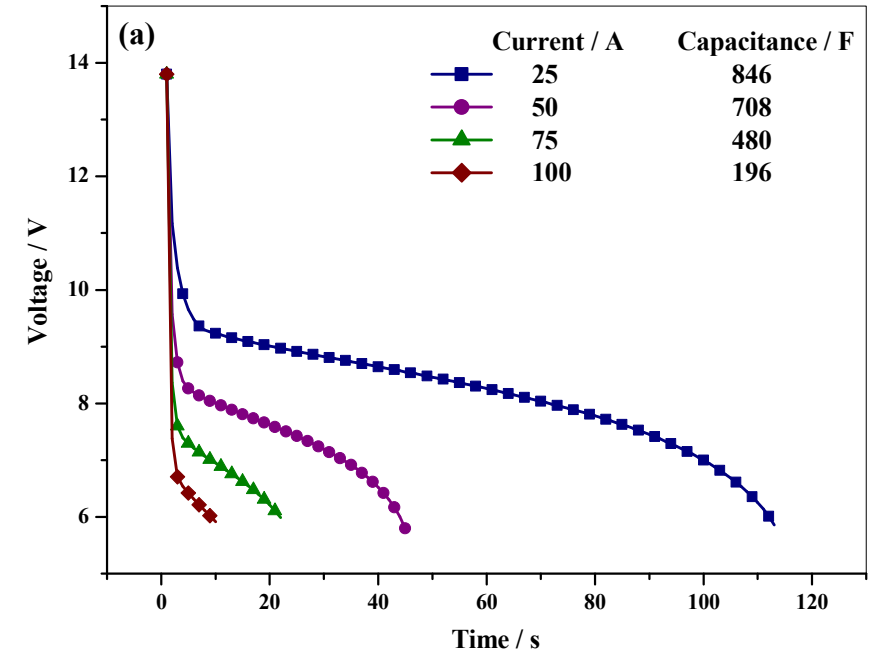

(a)
Current
Capacitance
3 A
1.38 kF
6 A
1.36 kF
9 A
1.34 kF
12 A
1.31 kF
15 A
1.25 kF
Voltage / V
Time / s
(b)
Current
Capacitance
3 A
2.45 kF
6 A
2.45 kF
9 A
2.42 kF
12 A
2.38 kF
15 A
2.31 kF
Voltage / V
Time / s

Fig.. 2


(a)
Current / A
Capacitance / F
25
846
50
708
75
480
100
196
Voltage / V
Time / s
14
12
10
8
6
0
20
40
60
80
100
120

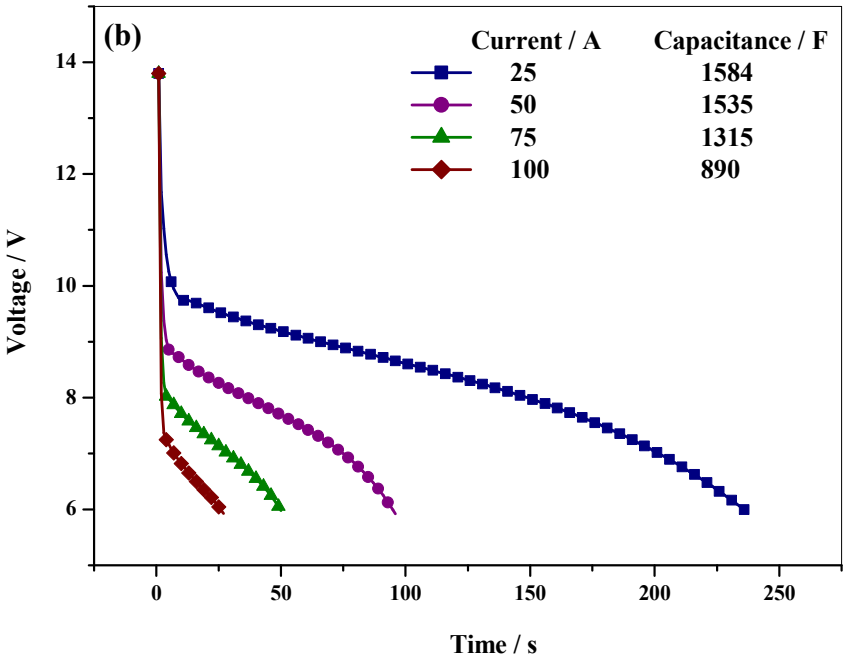
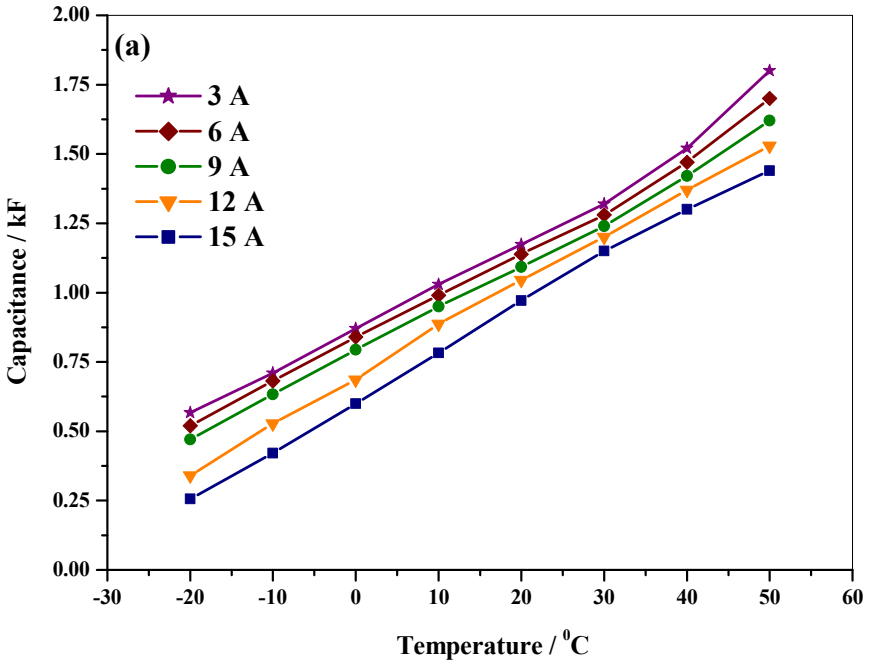

(b)
Current / A
Capacitance / F
25
1584
50
1535
75
1315
100
890
Voltage / V
Time / s
14
12
10
8
6
0
50
100
150
200
250

Fig. 3


(a)
3 A
6 A
9 A
12 A
15 A
Capacitance / kF
Temperature / ^{0}C
2.00
1.75
1.50
1.25
1.00
0.75
0.50
0.25
0.00
-30
-20
-10
0
10
20
30
40
50
60

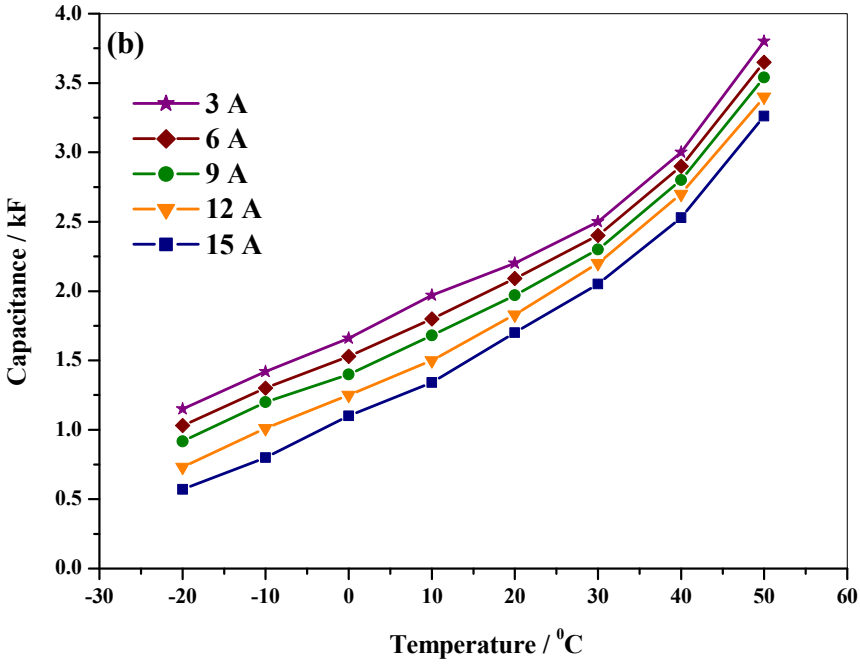

(b)
3 A
6 A
9 A
12 A
15 A
Capacitance / kF
Temperature / ^{0}C
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-30
-20
-10
0
10
20
30
40
50
60

Fig. 4

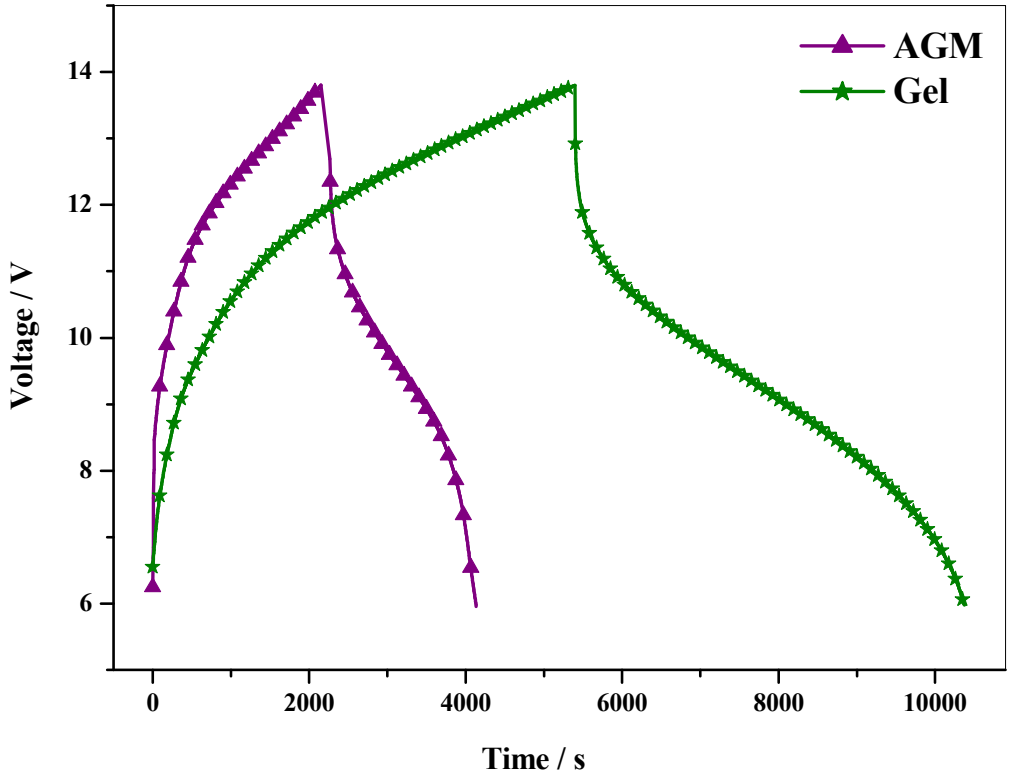


Fig. 5

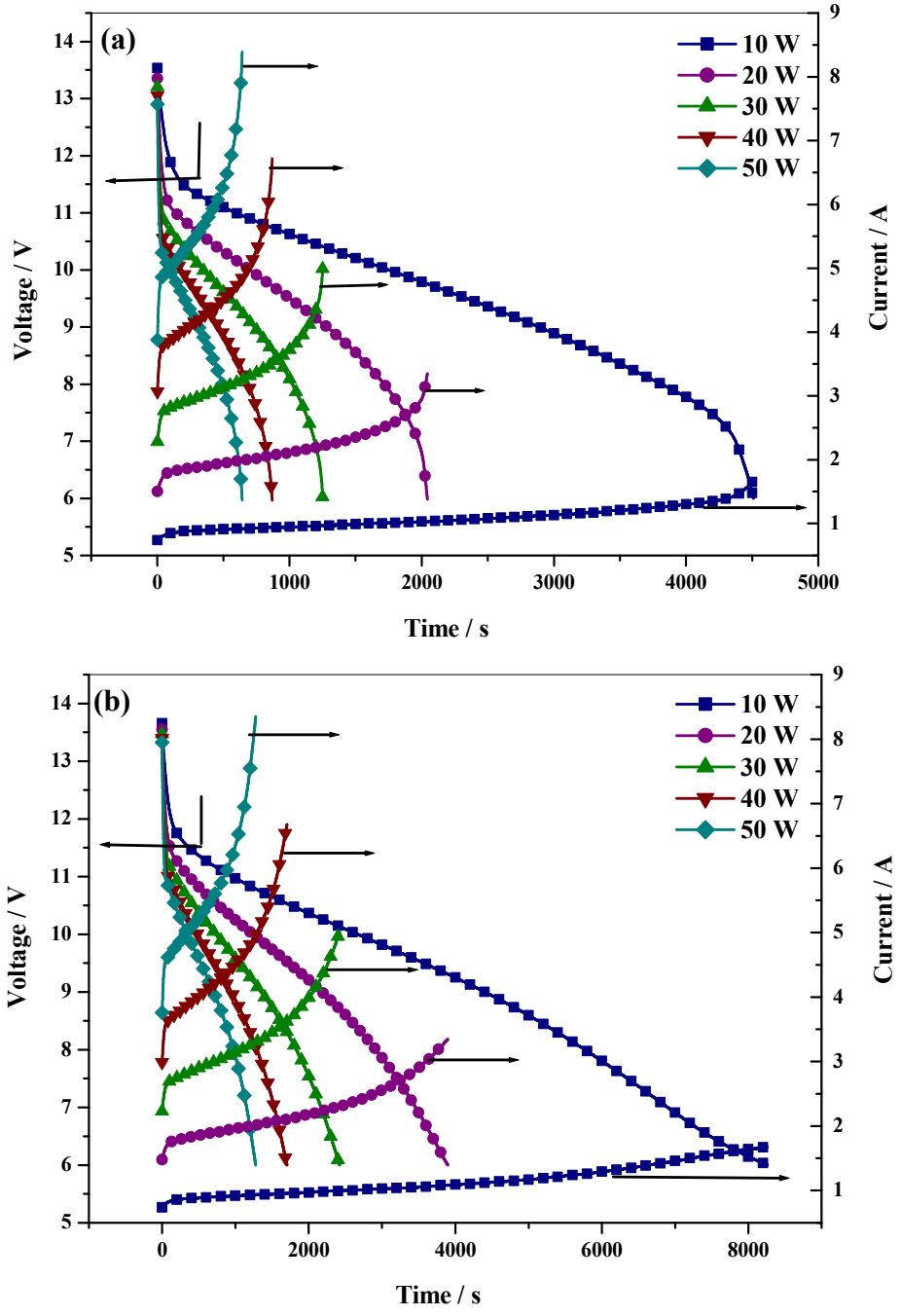

(a)
10 W
20 W
30 W
40 W
50 W
Voltage / V
Current / A
Time / s
(b)
10 W
20 W
30 W
40 W
50 W
Voltage / V
Current / A
Time / s

Fig . 6

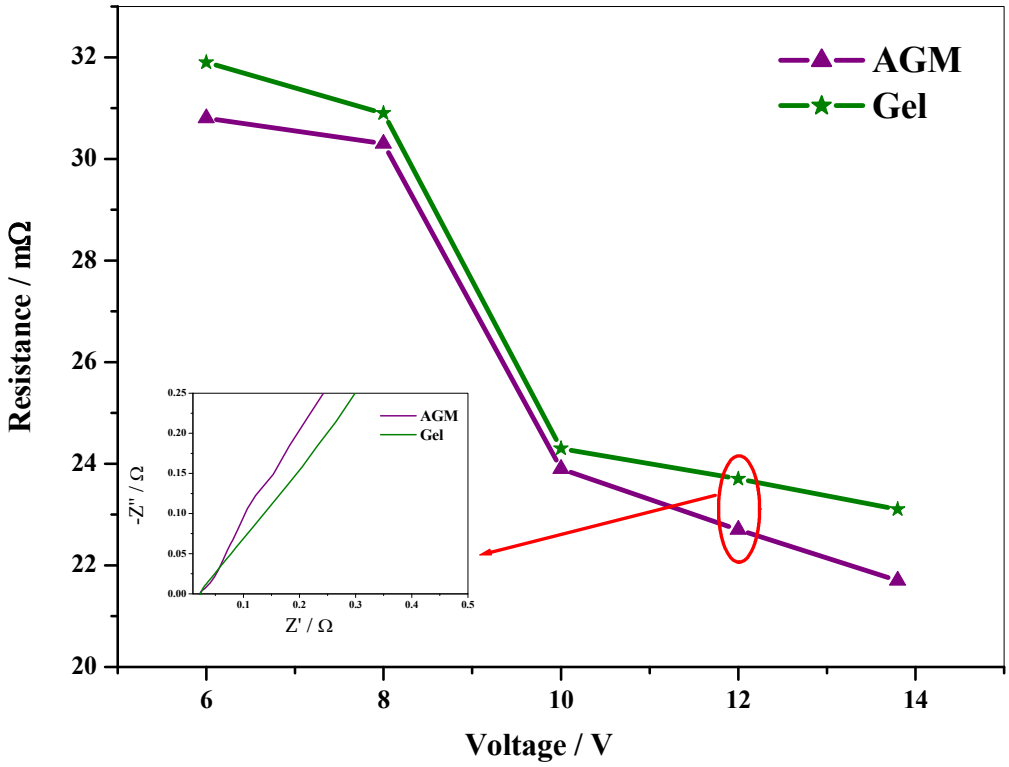

AGM
Gel
Resistance / mΩ
Voltage / V
32
30
28
26
24
22
20
6
8
10
12
14
-Z'' / Ω
Z' / Ω
0.25
0.20
0.15
0.10
0.05
0.00
0.1
0.2
0.3
0.4
0.5

Fig. 7

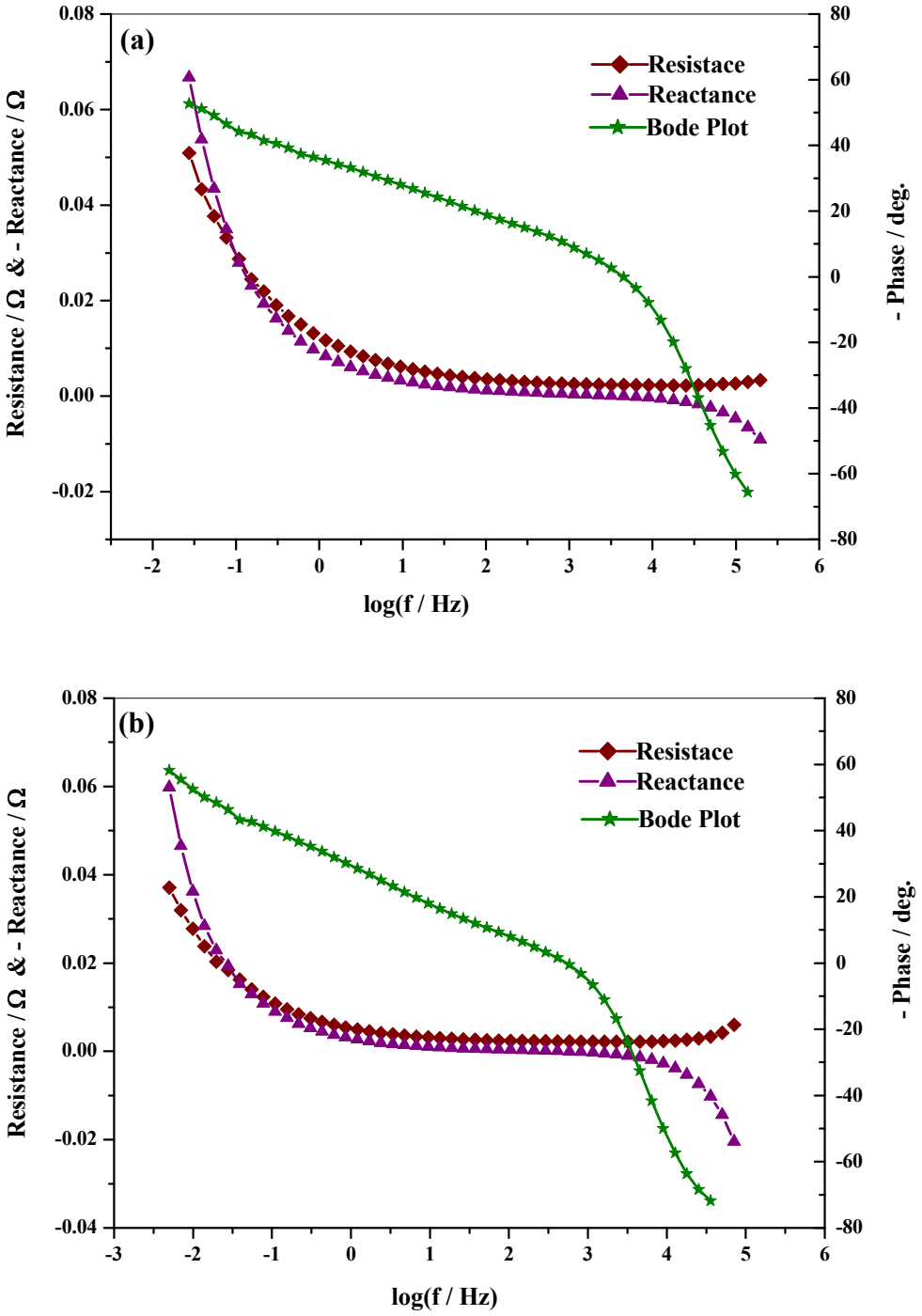

(a)
Resistace
Reactance
Bode Plot
Resistance / Ω & - Reactance / Ω
- Phase / deg.
log(f / Hz)
(b)
Resistace
Reactance
Bode Plot
Resistance / Ω & - Reactance / Ω
- Phase / deg.
log(f / Hz)

Fig. 8

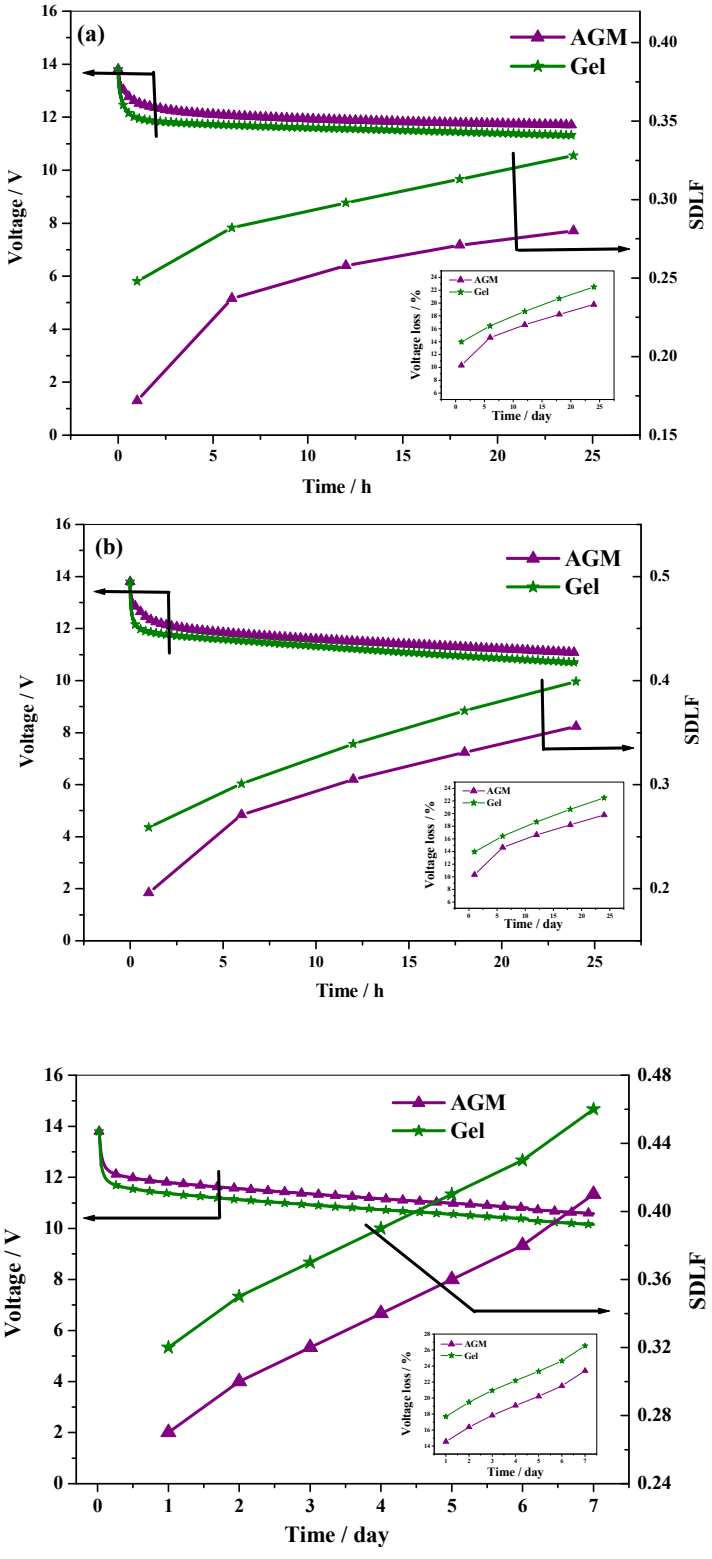

(a)
AGM
Gel
Voltage / V
SDLF
Time / h
Voltage loss / %
Time / day
(b)
AGM
Gel
Voltage / V
SDLF
Time / h
Voltage loss / %
Time / day
AGM
Gel
Voltage / V
SDLF
Time / day
Voltage loss / %
Time / day

Fig. 9

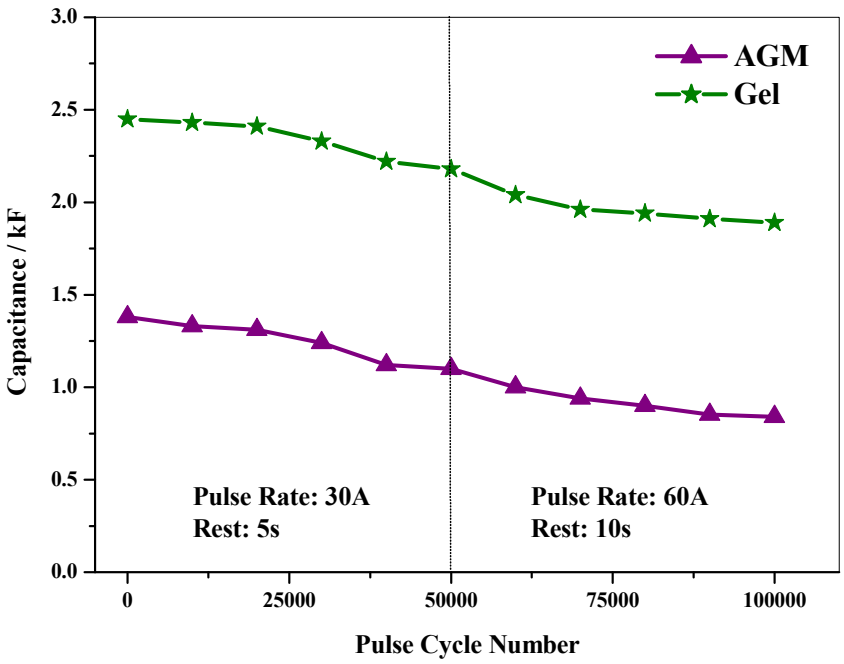

AGM
Gel
Capacitance / kF
Pulse Cycle Number
Pulse Rate: 30A
Rest: 5s
Pulse Rate: 60A
Rest: 10s
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0
25000
50000
75000
100000

Fig. 10